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PHOTOCHEMICAL PROCESSES DURING IRRADIATION OF CRUDE OIL IN TWO-PHASE SYSTEM “CRUDE OIL + WATER”

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Abstract: Photochemical transformation of petroleum hydrocarbons, n-alkanes, polycyclic and mono-aromatic hydrocarbons under the influence of UV radiation of a mercury lamp have been studied by chromatography and UV spectroscopy. It has been established the kinetic regularities of the formation of abovementioned hydrocarbons within the irradiation up to 90 min at $2x10^{15}$ photon/s UV-light intensity in various concentrations of crude oil up to 5000 ppm on the water surface. A mechanism of possible photochemical processes is discussed.

Keywords: crude oil, photochemical processes, n-alkanes, petroleum hydrocarbons, polycyclic and mono-aromatic hydrocarbons

1. Introduction

Photochemical degradation of crude oil in an aqueous medium is one of the physicochemical processes, taking place under the influence of UV part of solar radiation and constitutes about 10% of oil conversion in case of oil film on the surface of seawater. Degradation of crude oil occurs under the influence of various physical factors - including the effects of temperature, wind speed, chemical composition and the biological state of seawater. Simultaneous influence of the abovementioned factors makes it very difficult to clarify the mechanism of degradation process of crude oil. Taking into account the abovementioned features of photochemical degradation, it is expedient to study model system consisting of crude oil and distilled water.

This work is devoted to the study of photochemical processes under the influence of UV radiation in model system of crude oil – water.

2. Methods of experiment

Crude oil in an amount of 0.1÷0.5 ml was added to 40 ml of distilled water. Two-phase systems were prepared by placing them in quartz ampoules in a volume of 80 ml. Under the experimental conditions, crude oil creates a 0.1-0.5 mm thick film on the water surface.

Irradiation was conducted under the influence of the entire spectrum of a mercury lamp PRK-4, which has a resonance line in the region 223-546 nm and a continuous spectrum in the region of >546nm [4]. Irradiation of ampoules was carried out under the condition, in which the surface of irradiated part of the samples was maximal. The irradiation period was up to 90 min, the intensity of UV part of radiation was calculated on acetone actinometry and was $5x10^{15}$ quanta/sec.

Samples were cooled by air flow and the irradiation temperature did not exceed 30°C.

The oil components were analyzed after the extraction before and after irradiation. In this paper, chromatographic analyzes were carried out for the total amount of petroleum products, n-alkanes, polycyclic aromatic hydrocarbons.

Polycyclic analysis – Poly-aromatic hydrocarbons were analyzed on a gas chromatograph Pegasus GCxGC TOF-MS on a capillary column Rxi-5 MS with a length of 30 mx 0.25 mm ID. Temperature of the injector was 300°C. The temperature mode was programmed as follows. Heating was carried out from 70°C to 180°C at a rate of 85°C/min, then heated up to 230°C at a rate of 3°C/min, maintained at this temperature for 7 minutes, then heated up to 280°C at a rate of

28°C/min, this temperature was maintained for 10 minutes. Then it was heated up to 300°C at a rate of 14°C/min, this temperature was maintained for 3 minutes. Helium is used as the gas carrier. The gas carrier velocity was 50 ml/min, in a column 2 ml/min. The calibration was carried out using a standard solution in dichloromethane.

Analysis of n-alkanes and petroleum products – n-alkanes and petroleum products were analyzed on a Shimadzu GC-2010 PLUS gas chromatograph on a capillary column Rxi-5 MS with a length of 30 mx 0.25 mm ID. The temperature of the injector was 280°C, of the detector - 350°C. The temperature mode is programmed as follows. Temperature of 60°C was maintained for 2 minutes, then heated up to 195°C at a rate of 5°C/min. Then it was heated up to 350°C at a rate of 30 °C/min, this temperature was maintained for 15 minutes. Helium is used as a gas carrier. The gas carrier velocity was 8.6 ml/min, in a column 1.11 ml/min. Nitrogen (30ml/min) was used as the gas controller. The calibration was carried out using a standard solution in hexane.

Analysis of aromatic hydrocarbons – Mono-aromatic hydrocarbons were analyzed on a Shimadzu GC-2010 PLUS gas chromatograph on a capillary column Rxi-5 MS with a length of 30 mx 0.25 mm ID. The injector temperature was 230°C, of detector - 300°C. The temperature mode is programmed as follows. Temperature of 40°C was maintained for 8 minutes, then heated up to 120°C at a rate of 10°C/min. Helium was used as a gas carrier. The gas carrier velocity was 6.2 ml/min, in a column 1.6 ml/min. Nitrogen (25 ml/min) was used as the gas controller. The calibration was carried out using a standard solution in dichloromethane.

The absorption spectra of water part of the samples were also taken on a UV-VIS Cary-50 spectrophotometer.

Products of photochemical transformations and identification of oil components were investigated by chromatographic methods EPA D 8270 and ISO 11423-2. The results were shown in the following tables.

3. Results and discussion

1. Photochemical processes during irradiation of model aqueous solutions in the presence of crude oil.

Before the photochemical experiments, crude oil samples taken from the Dubandi terminal were analyzed; the results were given in the table, which include physical parameters, such as kinematic viscosity, density, and organic components.

Table 1. *Identified components in TPH*

	Identified components	Concentration (mg/l)
TPH	Octane	86.5
	Nonane	458.6
	Decane	426.1
	Undecane	513.7
	Dodecane	503.1
	Tridecane	665.8
	Tetradecane	423.5
	Pentadecane	316.7
	Hexadecane	177.1
	Heptadecane	426.3
	Pristane	-
	Octadecane	356.9
	Phytane	69.1

	Nonadecane	120.0
	Eicosane	-
	Docasane	-
	Tricosane	-
	Tetracosane	-
	Pentocosane	-
	Heneicosane	-
	Hexacosane	-
	Heptacosane	-
	Octacosane	-
	Hentricontane	-
	Dotriacontane	-
	Tritriacontane	-
	Pentotricontane	-
	TOTAL	**4543.4**

Table 2. *Identified components in PAH*

	Identified components	**Concentration (mg/l)**
PAH	Naphthalene	325.64
	Acenaphthylene	5.146
	Acenaphthene	18.714
	Fluorene	107.608
	Phenanthrene	236.998
	Anthracene	57.834
	TOTAL	**751.94**

Table 3. *Identified components in BTEX*

	Identified components	**Concentration (ppm)**
BTEX	Benzene	-
	Toluene	-
	Ethylbenzene	21.0
	m-, r-xylene	-
	o- xylene	71.5
	TOTAL	**92.4**

Table 4. *Physical properties of crude oil*

Temperature °C	**Kinematic viscosity cCT**	**Density, kg/m^3**
20	-	866
25	18.147	867
37.8	11.342	864
50	7.56	-

The study of photochemical degradation of crude oil components in two-phase systems based on distilled water was carried out as follows: Crude oil in the amount of 0.1, 0.2 and 0.5 ml and distilled water in an amount of 40 ml was poured into the 80 ml ampoule. Under these conditions, the geometric thickness of the oil film was 0.1-0.5 mm.

Table 1 shows the results of photolysis of two-phase system under the influence of UV radiation of a mercury lamp. It has been studied the changes in the concentration of TPH, n-alkanes, PAH and BTEX depending on irradiation period up to 90 min for a system containing 5000 ppm of crude oil.

Table 4. *Dependence of concentration of TPH, n-alkanes, PAH and BTEX on irradiation period*

Period, min	***0***	***15***	***40***	***60***	***90***
TPH (mg/l)	336.529	1211.105	937.178	907.223	1240.683
n-alkanes (mg/l)	3.663	6.220	7.599	7.159	3.356
PAH (mkg/l)	3324.53	284.295	1117.453	1203.874	1173.610
BTEX (mg/l)	1.240	1.606	1.863	1.824	2.213

As it can be seen from the table, the total concentration of petroleum products increases with the increase of dose up to an irradiation period of 15 minutes, then there is observed the formation of stationary concentration up to 60 minutes of irradiation. Further increase in irradiation period leads to an increase in the total concentration of petroleum products. In contrast to oil products, the concentration of n-alkanes increases up to 40 minutes. Further increase in the irradiation period leads to a decrease in the concentration of n-alkanes. The concentration of polycyclic aromatic hydrocarbons and aromatic hydrocarbons increase with the increasing irradiation period.

The change in the total concentration of petroleum products, polycyclic aromatic hydrocarbons and aromatic hydrocarbons from the irradiation period (15 minutes) depends on the concentration of crude oil: the increase in the irradiation period leads to an increase in the total concentration of petroleum products, to a decrease in the concentration of polycyclic aromatic hydrocarbons and n-alkanes during the photolysis of a system containing 0.1ml of crude oil. The antibate behavior of these dependences is observed in the photolysis of a system containing 0.5 ml of crude oil.

Among the n-alkanes, significant changes in concentration with increasing irradiation period take place for $C_{12}H_{26}$, $C_{14}H_{30}$, $C_{22}H_{46}$, $C_{24}H_{50}$, $C_{26}H_{54}$. Hydrocarbons such as $C_{10}H_{22}$, $C_{30}H_{62}$, $C_{32}H_{66}$, $C_{34}H_{70}$ are observed only during irradiation.

In the composition of BTEX, a significant change in the concentration is observed for ethylbenzene and o-xylene. The concentration of toluene does not change.

In the PAH, the concentration of fluoerene and phenantrene significantly increases with the irradiation period. Acenaphthene is observed only at long irradiation period.

A study of the concentration of petroleum hydrocarbons with the irradiation period of the abovementioned model systems was also carried out by the method of UV spectroscopy.

In Fig. 1 it has been shown the dependence of the absorption of oil components in the volume of water in the region of 200-800 nm at different irradiation periods of a model two-phase system of water + crude oil (5000 ppm).

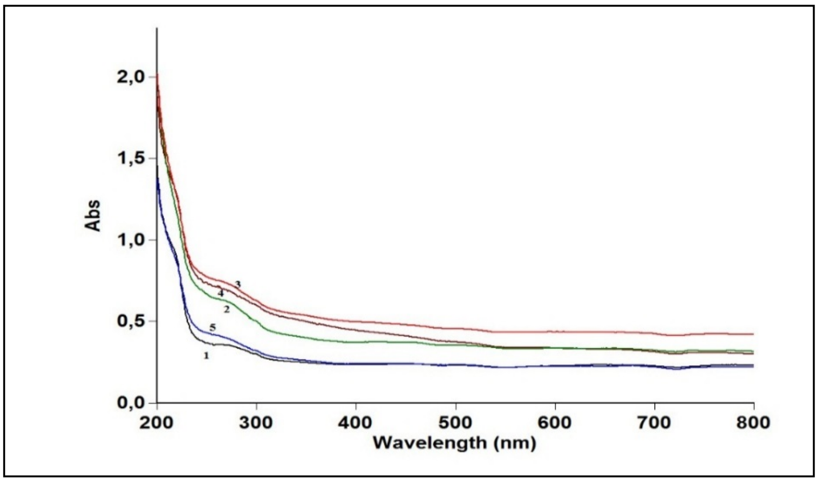

Fig. 1. Absorption of oil component in water volume in the region of 200-800 nm at different irradiation periods of model two-phase system of water + crude oil (5000 ppm) 1- original; 2- 15min; 3- 40min; 4- 60min; 5- 90min

As it is seen from the figure, the absorption (Abs) of products increases with the irradiation periods at the irradiation of model system, but the further increase of irradiation period leads to a decrease in absorption at t>40 min. The comparison of the obtained data with the data of Tab. 4 shows that, the observed dependence on the irradiation period is due to photolysis by photochemical decomposition of n-alkanes.

2. *Kinetic features of the change in the concentration of separate components of petroleum hydrocarbons during photolysis of the investigated systems.*

Figures 2 and 3 show the dependence of the change in the concentration of the BTEX and PAH components during irradiation of the model system of water + crude oil (5000 ppm).

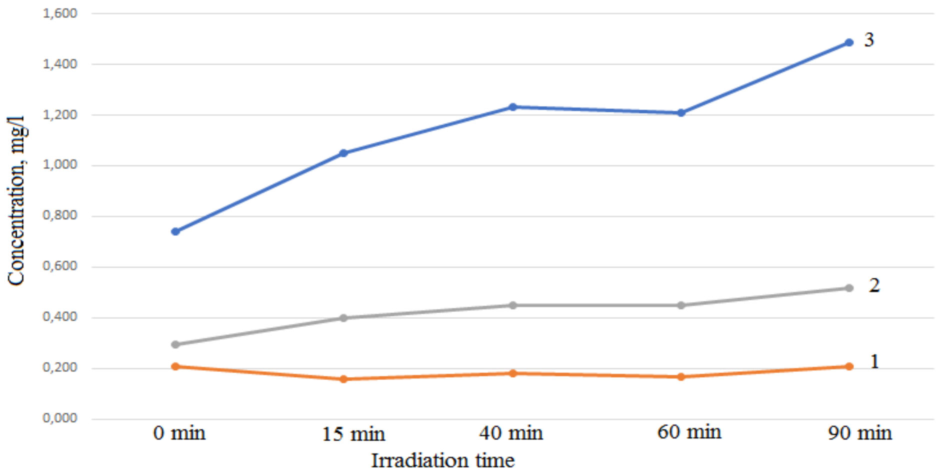

Fig. 2. Dependence of the concentration of BTEX components in water volume at different irradiation periods of model two-phase system of water + crude oil (5000 pmm).
1 - Toluene, 2 - ethylbenzene, 3 - o-xylene

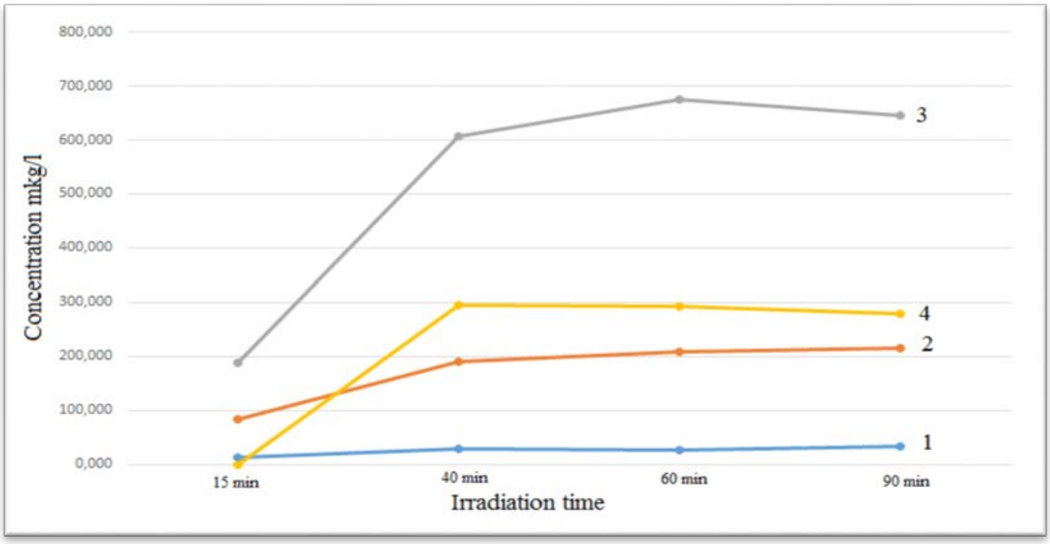

Fig. 3. Dependence of the concentration of PAH in water volume at different irradiation periods of model two-phase system of water + crude oil (5000pmm).
1- Acenaphthene, 2-Fluorene, 3-Phenantrene, 4-Anthracene

The observed regularities of photolysis of the crude oil + water system are associated with the absorption of UV radiation by molecules having absorption bands in the region > 220 nm. Such molecules are monoaromatic hydrocarbons, such as benzene, toluene, ethylbenzene, m-/r-xylene, o- xylene, as well as polycyclic aromatic hydrocarbons - acetonaphthalene, fluorene, phenanthrene are identified by us as crude oil components. For an example, the table shows the absorption maxima of o-xylene in the region of 288-400 nm.

Table 5. *The absorption maxima of o-xylene in the region of 288-400 nm [1]*

Wavelength, nm	**Maximum absorption**
288	1.000
300	0.200
325	0.050
350	0.010
400	0.005

The absorption spectra of benzene, toluene and ethylbenzene were shown in Fig. 4.

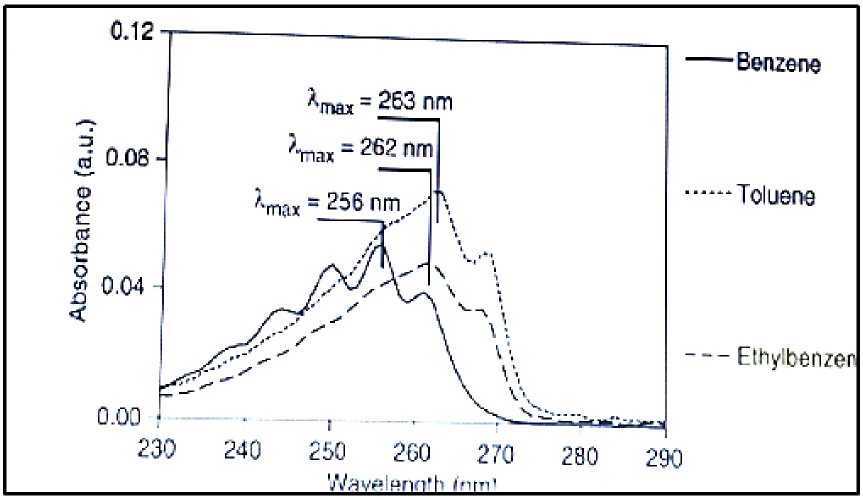

Fig.4. Absorption spectra of benzene, toluene and ethylbenzene [2]

As it is seen from fig. 4, the peak of absorption is within the range of 263, 262, 256 nm for benzene, toluene and ethylbenzene, respectively.

PAH is characterized by a band in the region of 220-340 nm [3]. Figure 5 shows the comparative absorption spectra of benzene, anthracene, and naphthalene.

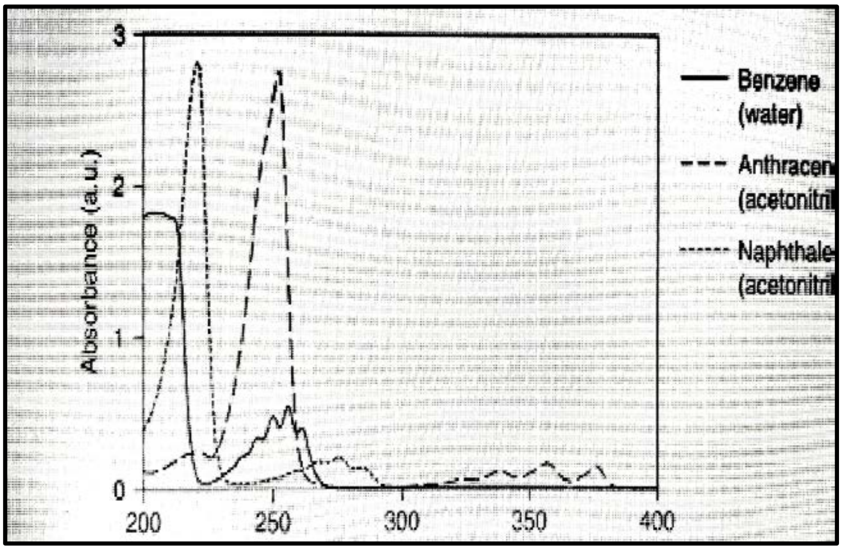

Fig. 5. Comparative absorption spectra of benzene, anthracene and naphthalene [2]

The observed changes in the concentration during the irradiation of these systems show the occurrence of direct photolysis reactions of molecules, absorbing UV radiation and the capture reaction of active particles presented in the system of compound molecules of the oil components.

In [5,6] it was demonstrated the role of PAH and aromatic compounds in the sensitization of saturated hydrocarbon components by transferring the energetically excited triplet states of PAH molecules and two quantum processes of excitation energy transfer

$$\mathrm{PAH(s)} \xrightarrow{h\upsilon} \mathrm{PAH(s^*)} \rightarrow \mathrm{PAH(T^*)} \xrightarrow{h\upsilon_2} \mathrm{PAH(T^*)} \xrightarrow{RH} \mathrm{PAH(s)} + \mathrm{RH^*} \rightarrow \mathrm{PAH(s)} + \mathrm{R^*} + \mathrm{H}$$

As a result, hydrocarbon molecules decompose to form additional and separation products, as well as oxidation in the presence of oxygen.

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ФОТОХИМИЧЕКИЕ ПРОЦЕССЫ ПРИ ОБЛУЧЕНИИ СЫРОЙ НЕФТИ В ДВУХФАЗНЫХ СИСТЕМАХ «СЫРАЯ НЕФТЬ+ВОДА»

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Резюме: Методами хроматографии и УФ-спектроскопии изучены фотохимические превращения нефтяных углеводородов, н-алканов, полициклических и моно- ароматических углеводородов под действием УФ-излучения ртутной лампы. Установлены кинетические закономерности образования вышеуказанных углеводородов при облучении до 90 мин при интенсивности УФ-света 2x10^{15} фотон/с при разных концентрациях сырой нефти до 5000 ppm на поверхности воды.Обсуждаются механизм возможных фотохимических процессов.

Ключевые слова: сырая нефть, фотохимические процессы, н-алканы, нефтяные углеводороды, полициклические и моно- ароматические углеводороды

İKİFAZALI “XAM NEFT+SU” SİSTEMİNDƏ XAM NEFTİN ŞÜALANDIRILMASI ZAMANI BAŞ VERƏN FOTOKİMYƏVİ PROSESLƏR

T.S. İdrisov, M.Ə. Qurbanov, Ü.A. Quliyeva

Xülasə: Xromatoqrafiya və UB-spektroskopiya metodları ilə neft karbohidrogenlərinin, n-alkanların, politsiklik və mono- aromatik karbohidrogenlərin civə lampasının UB- şüalarının təsiri altında fotokimyəvi çevrilmə prosesləri öyrənilmişdir.UB- şüalanmanın intensivliyinin 2x10^{15} foton/san qiymətində yuxarıda qeyd edilən karbohidrogenlərin 90 dəq şüalanma müddətinə kimi kinetik qanunauyğunluqları və mümkün fotokimyəvi proseslərin mexanizmi öyrənilmişdir.

Açar sözlər: xam neft, fotokimyəvi proseslər, n-alkanlar, neft karbohidrogenləri, politsiklik və mono-aromatik karbohidrogenlər